

SYNTHESIS OF SOME DISUBSTITUTED STYRENES

BY

JAMES HENRY SAUNDERS

B.S., University of Kentucky, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
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ACKNOWLEDGMENT

The author wishes to express his appreciation for the advice and guidance of Professor C. S. Marvel in carrying out this work.

He also wishes to express his thanks to Dr. R. D. Deanin for help in copolymerization studies, and to the B. F. Goodrich Company for evaluation of the copolymers.

This work was done under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.



SYNTHESIS OF SOME DISUBSTITUTED STYRENES

INTRODUCTION

The synthetic rubber most widely used for the production of tires in the United States, GR-S, has certain defects which cause it to be inferior to natural rubber in some properties. Because of the low supply of natural rubber and the correspondingly great demand for a satisfactory synthetic rubber during the war it became essential to attempt to correct those defects. One approach to this subject was the observation of the effect of using substituted styrenes in the place of one of the comonomers, styrene. In connection with this program five disubstituted styrenes, 3,5-, 2,4-, 2,5-, and 3,4-dimethylstyrene and 3,4-dichlorostyrene, have been prepared in quantities sufficient to permit a cursory examination of their copolymers. The polymers and copolymers of these compounds have been prepared and characterized.

DISCUSSION OF RESULTS

3,5-Dimethylstyrene has been prepared from mesitylene, which was oxidized with manganese dioxide and sulfuric acid according to the procedure of Weiler¹ to produce 3,5-dimethyl benzaldehyde. This aldehyde was then converted to 3,5-dimethylphenylmethylcarbinol by treatment with methyl magnesium iodide. Dehydration over fused potassium acid sulfate by the method of Marvel and Schertz² resulted in the formation of 3,5-dimethylstyrene.

2,4-, 2,5-, and 3,4-Dimethylstyrene were made from *meta para*, and *ortho*-xylene, respectively. Acetylation by the method of Perkin and Stone³ gave the corresponding substituted acetophenones. Reduction of the ketones to the carbinols with aluminum isopropoxide was accomplished using the method of Marvel and Overberger.⁴ Under the conditions used the reduction of 3,4-dimethylacetophenone produced a large quantity of high-boiling material, apparently

2,4-di(3,4-dimethylphenyl)-4-hydroxybutene-2, the result of a dyponone type condensation, followed by reduction of the carbonyl group. Reduction of 3,4-dimethylacetophenone with Raney nickel gave a good yield of the carbinol. Dehydration of the carbinols to form the styrenes was accomplished by the method used for the 3,5-dimethylstyrene.

3,4-Dichlorostyrene was prepared by a new procedure. Alkylation of *ortho*-dichlorobenzene with ethyl bromide produced 3,4-dichloroethylbenzene, which was chlorinated on the side chain. Direct dehydrohalogenation of 3,4-dichloro- α -chloroethylbenzene failed, but treatment of this compound with potassium acetate in acetic anhydride converted it to the acetate of 3,4-dichlorophenylmethylcarbinol. The styrene was obtained by prolysis of the ester at 575°.

A polymer of each of the substituted styrenes was made by exposing the monomer to ultraviolet light for one to three days. Copolymers of each were made by emulsion copolymerization with butadiene. Industrial evaluation indicated that the copolymers of the dimethylstyrenes with butadiene were little better than ordinary butadiene-styrene copolymers.⁵ Preliminary investigation indicated that the 3,4-dichlorostyrene-butadiene copolymer was superior; but further tests on copolymers containing different percentages of 3,4-dichlorostyrene indicated that the improvement was not enough to warrant semi-works development.⁵

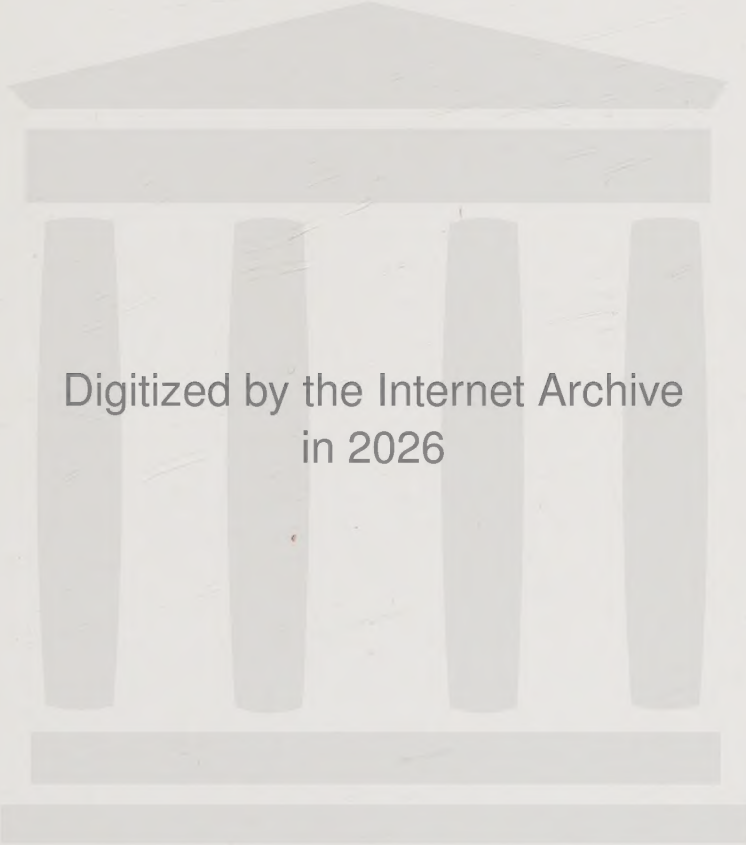
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VITA

The author was born May 3, 1923, in Ames, Iowa. He attended the public schools in Hopkinsville, Kentucky, and was graduated from high school in 1941. He then studied at the University of Kentucky where he received the Bachelor of Science degree in chemistry in 1944. At that time he entered the graduate school of the University of Illinois, where he was employed as a research assistant on the Rubber Research Program. He held a fellowship granted by the Abbot Laboratories from October, 1944, to June, 1944, at which time he returned to the staff of the Rubber Research Program.



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